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Short-range structure of β -V₂D: Pair distribution function analysis of x-ray and neutron diffraction

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X-ray and neutron diffraction experiments using pair distribution function (PDF) analysis were used to elucidate the short-range structure of β -V₂D. The PDF obtained by x-ray diffraction indicated the displacement of the vanadium atoms from the ideal body-centered-tetragonal lattice positions; the displacement was evaluated to be 0.008(2) nm. Reverse Monte Carlo simulation based on x-ray and neutron PDFs was also used to determine the locations of the deuterium atoms. Results suggest that the deuterium atoms are displaced from the centers of the octahedral sites and are surrounded by four vanadium atoms at equal average distances.

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I. INTRODUCTION

Vanadium-hydrogen (deuterium) systems are of interest from both technological and fundamental points of view. The structure of β -V₂D has been investigated by a number of researchers.^{1–4} Somenkov *et al.* first reported that deuterium atoms are ordered in the octahedral sites of the body-centered-tetragonal (bct) vanadium lattice at room temperature.¹ This structure is described by the monoclinic cell (C_m) defined by $A=C=(a_0^2+b_0^2)^{1/2}$, $B=a_0$, and $\beta=94.6^\circ$, as shown in Fig. 1. Almost the same structural models were reported by Westlake *et al.*² and Asano and Hirabayashi.³ In addition, the results of both studies showed that a small amount of deuterium atoms could occupy the tetrahedral sites. Furthermore, Kajitani and Hirabayashi reported that the distribution of the deuterium atoms in β -V₂D extends over the four tetrahedral sites, using neutron diffraction data with a single crystal.⁴

In addition to the location of the deuterium atoms, much interest has been focused on the displacement of the vanadium atoms from the ideal lattice positions, induced by interstitial deuterium atoms. The displacement of the vanadium atoms in β -V₂D has been studied using single-crystal x-ray diffraction.^{5–7} Metzger *et al.* first reported the displacement of vanadium atoms in β -V₂D.⁵ Later, Jo *et al.* estimated the displacement to be 0.015 nm, based on the intensities of superlattice refraction.⁶ Noda *et al.* later investigated the host vanadium structure in β -V₂D and estimated the displacement to be 0.010 nm,⁷ which is much smaller than the value obtained by Jo *et al.*⁶

All of these structural investigations of β -V₂D were conducted using a conventional approach based on Bragg peaks. Therefore, the information obtained is for the average structures. If the deuterium atoms occupy the centers of the octahedral sites in the bct lattice, they are surrounded by four vanadium atoms at a distance 0.214 nm and two vanadium atoms at a distance 0.175–0.180 nm. There is some question as to whether such interstitial sites for deuterium are stable.

Fukai and Sugimoto have calculated a potential profile of the self-trapped state of deuterium in the vanadium lattice from the ground-state wave function.^{8,9} They showed that the wave function of deuterium extends over some region around the octahedral sites, bearing four maxima reminiscent of the tetrahedral sites, and also emphasized that it is meaningless to treat the interstitial sites for hydrogen (deuterium) as geometrical points.

Since the stability of the occupational sites of deuterium is strongly related to the short-range interaction between vanadium and deuterium, it is clearly important to study the short-range structure. In this work, therefore, the short-range structure of β -V₂D was investigated using a pair distribution function (PDF) technique derived from the Fourier transformation of a structure factor obtained by x-ray and neutron diffraction. PDF analysis of x-ray or neutron diffraction data has been used to investigate the short-range structure of non-crystalline materials such as liquids and glasses.¹⁰ Recently, PDF analysis has also been applied to the study of crystalline materials in order to obtain direct information on local atomic correlations.^{11–13} However, PDF analysis only yields one-dimensional information. Therefore, complementary use of x-ray and neutron diffraction, by taking advantage of the different scattering factors, is useful and necessary in PDF analysis. From this point of view, the V-D system is an extremely good example because the atomic scattering factor of the vanadium atoms is much larger than that of the deuterium atoms for x-ray diffraction and the coherent scattering length of the deuterium atoms is much larger than that of the vanadium atoms for neutron diffraction. Therefore, x-ray and neutron diffraction data for the V-D sample give completely different types of information, thus allowing the atomic correlations to be determined. Consequently, the combined use of x-ray and neutron diffraction techniques can be a very powerful means to elucidate the structure of the V-D sample. In addition, we used reverse Monte Carlo (RMC) modeling,¹⁴ a well-established and effective method for constructing three-dimensional atomic arrangements of crystalline¹⁵ and disordered materials. The application of

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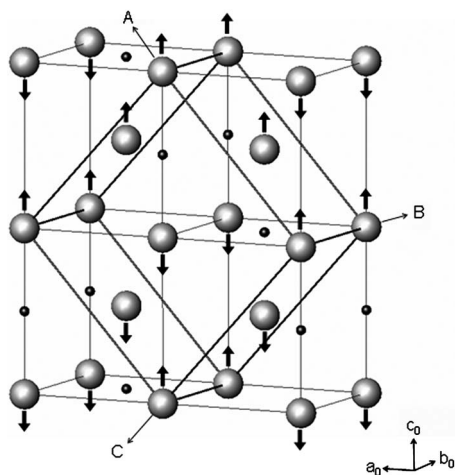


FIG. 1. Structure of β -V₂D proposed by Somenkov *et al.* (Ref. 1). Large spheres are vanadium atoms and small spheres are deuterium atoms. The bct vanadium lattice is depicted by thin lines. The arrows indicate the direction of the displacement of vanadium atoms.

RMC modeling based on x-ray and neutron data to β -V₂D provides detailed information on the locations of the deuterium atoms.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

A β -V₂D sample was prepared by directly reacting vanadium powder (Mitsuwa Pure Chemicals, 99.5%, 325 mesh) with deuterium gas (99.999%) using a Sieverts-type apparatus. A quantity of 3 g of vanadium powder was degassed at 1073 K for several hours under vacuum to below 10^{-4} Pa inside a quartz tube placed in an electric furnace. It was cooled to 773 K and reacted with deuterium gas, then cooled slowly to room temperature. The concentration of deuterium in the sample was evaluated from the absorbed deuterium gas and confirmed by quantitative elemental analysis at the Center for Organic Elemental Microanalysis, Kyoto University. The deuterium to vanadium ratio was determined to be D/V=0.50(2).

B. X-ray and neutron diffraction experiments

The x-ray diffraction measurement was carried out using a horizontal two-axis diffractometer with a photon energy of 61.57 keV ($\lambda=0.02014$ nm) on the BL04B2 beam line at the SPring-8 facility. After corrections for polarization, absorption,¹⁶ and Compton scattering,¹⁷ the scattering intensity, $I(Q)$, was converted to the structure factor, $S(Q)$, where $Q=4\pi \sin \theta/\lambda$.

The neutron diffraction measurement was carried out in the high intensity total scattering spectrometer (HIT-II) installed at the pulsed neutron source in the High Energy Accelerator Research Organization (KEK, Tsukuba, Japan). The alloy sample was placed into a vanadium cell with an inner diameter of 8.0 mm and a thickness of 0.025 mm. The $S(Q)$ was derived by applying various corrections for the background, absorption,¹⁸ and multiple scattering,¹⁹ as well as normalization with a vanadium rod.

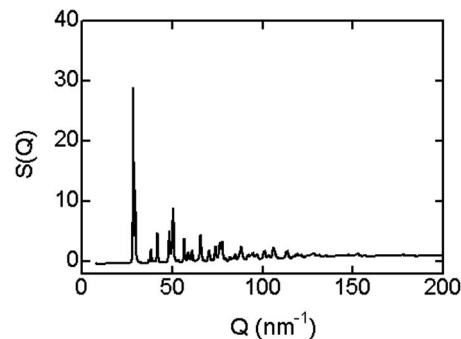


FIG. 2. Structure factor, $S(Q)$, for β -V₂D observed by x-ray diffraction with a photon energy of 61.57 keV ($\lambda=0.02014$ nm).

$S(Q)$ was analyzed by the Faber–Ziman definition²⁰ as follows:

$$S(Q) = \frac{I(Q) - \{\langle b^2 \rangle - \langle b \rangle^2\}}{\langle b \rangle^2}, \quad (1)$$

and

$$\langle b^2 \rangle = \sum_i c_i b_i^2, \quad (2)$$

$$\langle b \rangle = \sum_i c_i b_i,$$

where c_i and b_i are the concentration and the coherent scattering length for neutron diffraction (or atomic scattering factor for x-ray diffraction) of the component atoms i , respectively. The pair distribution function, $g(r)$, can be derived from the Fourier transformation of $S(Q)$ as follows:

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho} \int_0^\infty Q[S(Q) - 1] \sin Qr dQ, \quad (3)$$

where ρ is the average number density of the atoms.

The pair distribution function, $g(r)$, of a V-D binary mixture can be described as a weighted sum of three partial pair distribution functions, $g_{i-j}(r)$,

$$g(r) = w_{V-V} g_{V-V}(r) + w_{V-D} g_{V-D}(r) + w_{D-D} g_{D-D}(r), \quad (4)$$

where w_{i-j} is the weighting factor defined as

$$w_{i-j} = \frac{c_i c_j b_i b_j}{\langle b \rangle^2}. \quad (5)$$

C. Reverse Monte Carlo modeling

RMC modeling¹⁴ was carried out by fitting to both x-ray and neutron $g(r)$ functions. A simulation box containing 3000 atoms with the appropriate composition and having periodic boundary conditions was used. To ensure a physically realistic configuration, the closest distances between two atoms (V-V, V-D, and D-D) were determined from the experimental $g(r)$ functions.

III. RESULTS AND DISCUSSION

A. Atomic arrangement of vanadium atoms

Figure 2 shows the structure factor, $S(Q)$, for β -V₂D

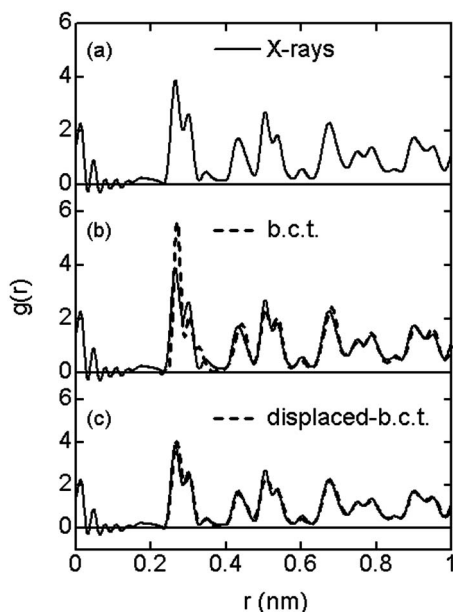


FIG. 3. (a) Pair distribution function, $g(r)$, for β -V₂D observed by x-ray diffraction. Pair distribution functions calculated by PDFfit program (Ref. 21) (broken lines) for: (b) the bct structure; (c) the configuration with displaced (0.008 nm) vanadium atoms, compared with the experimental $g(r)$ functions (solid lines).

observed by x-ray diffraction, and Fig. 3(a) shows the pair distribution function, $g(r)$, obtained by Fourier transformation of the x-ray $S(Q)$. The $g(r)$ shows three peaks at distances below 0.39 nm, which correspond to three kinds of V-V nearest neighbor correlations. The coordination number, calculated from the area under the $g(r)$ curve between 0.22 and 0.39 nm, was 14.3(5), which is consistent with the 14-fold nearest-neighbor coordination of the bct lattice. Nevertheless, the small peak at 0.346 nm in the $g(r)$ does not correspond to any atomic pair correlations in the bct structure.

Figure 3(b) shows the calculated $g(r)$ using the PDFfit program²¹ for the bct vanadium lattice, compared with the experimental $g(r)$. The calculated $g(r)$ for the bct lattice has three distances, which correspond to the correlations of eightfold, fourfold, and twofold vanadium atoms, respectively. Large differences in intensity can clearly be seen for the first and second peaks of the experimental and calculated $g(r)$ functions, with slight differences in the positions. Furthermore, a large discrepancy in both the position and the intensity of the third peak can be observed. The coordination number, calculated from the area under the small peak at 0.346 nm in the experimental $g(r)$, was 1.0(5). This result suggests a displacement of vanadium atoms from the average positions in the bct lattice in the direction of the c_0 axis (arrows shown in Fig. 1), as reported in previous reports⁵⁻⁷; however, the average displacement from the position of the third peak in the experimental $g(r)$ was 0.008(2) nm.

Figure 3(c) shows the calculated $g(r)$ for the displacement configuration of vanadium atoms by using the PDFfit program,²¹ compared with the experimental $g(r)$. These values are in much better agreement than those in the structural model based on the bct vanadium lattice. The displacement

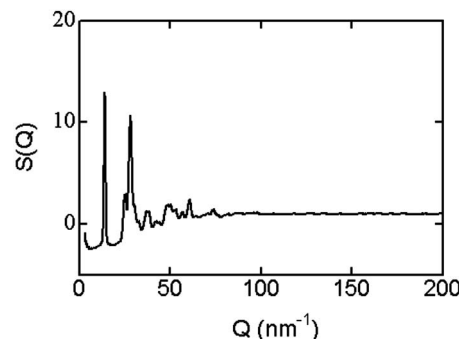


FIG. 4. Structure factor, $S(Q)$, for β -V₂D observed by neutron diffraction.

obtained in this work [0.008(2) nm] is much smaller than that reported by Jo *et al.* (0.015 nm),⁶ but close to that reported by Noda *et al.* (0.010 nm).⁷

B. Location of deuterium atoms

Figure 4 shows the structure factor, $S(Q)$, for β -V₂D observed by neutron diffraction. The corresponding pair distribution function, $g(r)$, is shown in Fig. 5(b). Since the coherent neutron scattering length of vanadium (0.382×10^{-15} m) is negative and much smaller than that of deuterium (6.67×10^{-15} m), positive peaks in the $g(r)$ are D-D correlations and negative peaks are V-D correlations. If the deuterium atoms are located in the octahedral sites, two negative peaks would be expected at 0.173 and 0.214 nm in the neutron $g(r)$. However, no negative peaks could be observed at these positions. A negative peak corresponding to the V-D correlation can be observed at 0.181 nm. The coordination number of vanadium atoms around a deuterium atom, calculated from the area under the negative peak, was 4.1(2). These results suggest that the deuterium atoms occupy the tetrahedral sites rather than the octahedral sites. In order to obtain more information on the location of deuterium atoms, we used the RMC method.

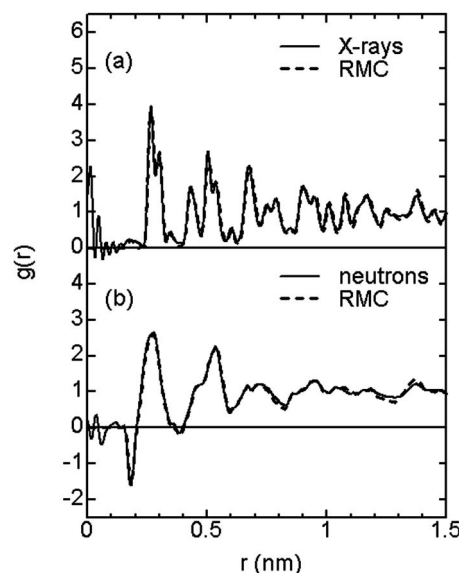


FIG. 5. Pair distribution functions, $g(r)$, observed by x-ray and neutron diffraction for β -V₂D, compared with the x-ray and neutron diffraction $g(r)$ functions calculated from the RMC model (broken lines), respectively.

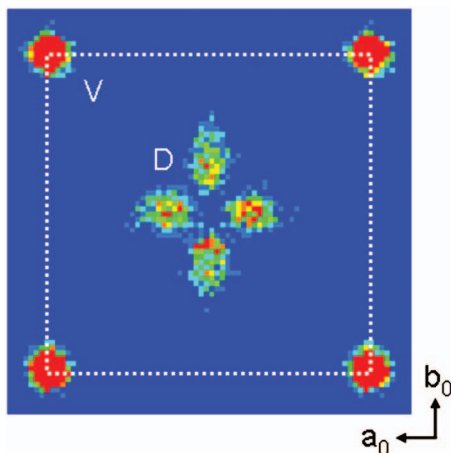


FIG. 6. (Color) Average density distribution of deuterium and vanadium atoms in the (001) planes of the bct lattice in β -V₂D derived from a 0.04 nm thick slice of the RMC configuration.

A RMC fit was performed in real space using both x-ray and neutron $g(r)$ functions. The crystal structure of β -V₂D (as shown in Fig. 1), with displacement of the vanadium atoms [0.008(2) nm], was used as a starting configuration. Maximum moves for each atom in the RMC simulation were set to 0.002 nm to prevent deuterium atoms from switching to neighboring sites. Calculated x-ray and neutron $g(r)$ functions from the RMC model for β -V₂D are plotted in Figs. 5(a) and 5(b), respectively, together with the experimental $g(r)$ functions. The x-ray and neutron diffraction values were in good agreement with the experimental $g(r)$ functions in the region below 1.5 nm.

Figure 6 shows an average density distribution of deuterium atoms and vanadium atoms in the (001) planes of the bct lattice derived from a 0.04 nm thick slice of the RMC configuration. It is important to note that the density distribution of deuterium atoms has four maxima around the octahedral sites. These locations are seemingly the tetrahedral sites, but deviate from the normal positions of the tetrahedral sites. However, the deuterium atoms are surrounded by four vanadium atoms at equal distances because of the outward displacement of vanadium atoms in the direction of the c_0 axis.

The atomic arrangements in metal-deuterium systems are thought to strongly correlate with the interactions between the metal and deuterium atoms. If the deuterium atoms occupy the center of the octahedral sites in the bct lattice in β -V₂D, they are surrounded by four vanadium atoms at a distance 0.214 nm and two vanadium atoms at a distance

0.173 nm. The latter correlation distance is too short for the V-D distance when considering the atomic radii of vanadium and deuterium. In order to minimize the repulsion between vanadium and deuterium, the locations of the deuterium atoms deviate from the octahedral sites, accompanying the displacement of the vanadium atoms, while maintaining equal V-D distances.

IV. CONCLUSIONS

The short-range structure of β -V₂D at room temperature was determined from a PDF analysis using x-ray and neutron diffraction data. The displacement of the vanadium atoms from the ideal bct lattice positions was determined to be 0.008(2) nm from the x-ray PDF. The locations of the deuterium atoms were obtained using RMC simulation. The deuterium atoms were determined to occupy sites surrounded by four vanadium atoms at equal average distances.

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